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Energetics of Anionic Surfactant-Additive Systems at the Cloud Point[1]

Shaeel Ahmed Al-Thabaiti[a], Abdullah Yousif Obaid[a], Ziya Ahmad Khan[a], Tanweer Ahmad[b], Arniza Ghazali[b], and Kabir-ud-Din[c]

[a] *Department of Chemistry, King Abdul Aziz University, Jeddah 21413, Saudi Arabia*
[b] *School of Industrial Technology, Universiti Sains Malaysia, Penang 11800, Malaysia*
[c] *Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India*
e-mail: ziyaakhan@gmail.com

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Abstract—The energetics of clouding in anionic surfactant (SDBS) and tetrabutylammonium bromide system in the presence of additives, such as ureas, amino acids and sugars is reported. The change of standard Gibbs energy of solubilization (ΔG_s°) for all of the additives was found to be negative. The values of change of standard enthalpy (ΔH_s°) and that of standard entropy ($T\Delta S_s^\circ$) values were found to depend on the type and chemistry of the additive. The results were explained on the basis including chemistry of additives, their effect on water structure, and solubilization of additives either in the micellar or in aqueous phases.

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INTRODUCTION

Clouding is an inherent property of nonionic surfactant solutions. At the cloud point (CP), a homogeneous nonionic surfactant solution separates into two coexisting phases, one of which contains much of the surfactant, generally named as the surfactant-rich phase, while the other phase has largely water with surfactant concentration around its critical micelle concentration (cmc) [1]. This phase separation is reversible; that is, when temperature decreases below CP, the two-phase system merges into a single homogeneous phase.

Clouding is attributed to the efficient dehydration of hydrophilic portion of the micelle at higher temperature. An increase in temperature results in gradual removal of hydrated water from hydrophilic headgroups leading to van der Waals attraction between micelles to dominate and hence the clouding [2]. The CP value depends upon various factors including type of surfactant, surfactant concentration, and additives [3]. On the other hand, clouding phenomenon has not been observed in the case of totally charged micellar systems, as raising temperature allows increase in electrostatic repulsion between micelles due to an increase of counterion dissociation. Recently, clouding has been, however, reported for charged micellar systems upon addition of organic salts [4–10]. The role of these salts is to lower the net charge on micelles as well as to bridge them. Therefore, all the organic salts having counterions with enough hydrophobicity can be used as additives [11], which are adsorbed in certain amounts on the micellar surface. The temperature-dependent solubility of the remaining portion of counterions provides a route for binding the micelles [7].

However, the mechanism, which guides the phenomenon, remains obscure. The role of oscillations in the critical concentration and of micellar growth as mechanisms for the clouding phenomenon is still a controversial issue [12, 13]. It is well established that the addition of ionic surfactants increases the cloud points of their nonionic counterparts [14, 15] and this increase depends on composition of the mixed micelles. Valaulikar and Manohar [16] have demonstrated that the increase in cloud point can be described in terms of the surface charge per micelle, which is responsible for electrostatic repulsion between the micelles. This supports the viewpoint that micelle coalescence, rather than micellar growth, is responsible for the clouding process. Hence, if introduction of charge to a nonionic micelle inhibits phase separation, the depletion of charge on an ionic micelle could cause resumption of this process. Thus, the charge could be one of the factors to tune CP, especially in ionic micellar solutions.

The clouding of micelles is of practical interest in a route, by which the material can be solubilized in micelles and phase separated. Therefore, phenomenon of micellar clouding has been extensively employed to different extraction methods of separation and purification in chemical, pharmaceutical, mineral, and petroleum industries [17, 18].

[1] The article is published in the original.